REDOX POTENTIAL (EH) MEASUREMENT

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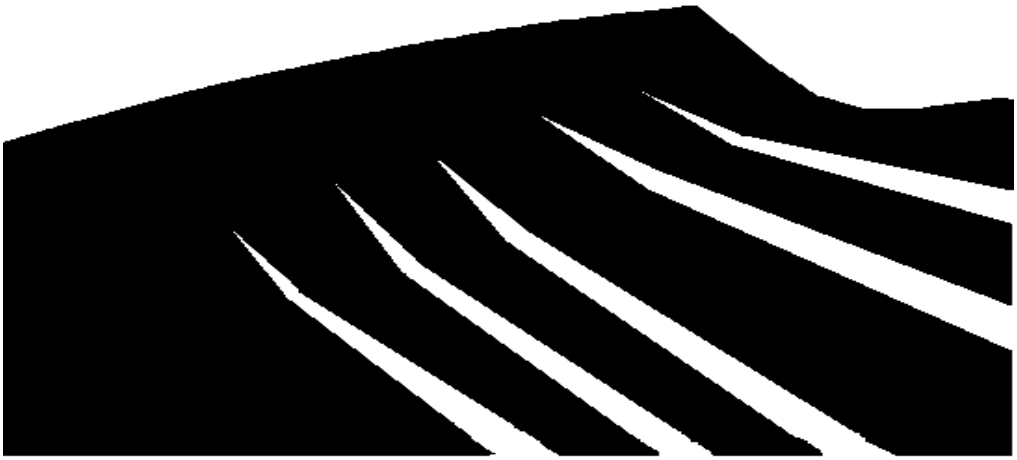

APPROVAL FOR RELEASE

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Los Alamos
Yucca Mountain Site
Characterization Project

HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	09/13/95		Initial Procedure
R1	12/10/96	All	Revised to comply with LANL-YMP-QP-06.3 requirements

REDOX POTENTIAL (Eh) MEASUREMENT

1.0 PURPOSE

The purpose of this detailed technical procedure (DP) is to describe the measurement of redox potential (Eh) of a solution by using a platinum combination redox electrode for experiments conducted at Los Alamos National Laboratory (Los Alamos) for the Yucca Mountain Site Characterization Project (YMP).

2.0 SCOPE

This procedure may be used to determine the Eh of solution or groundwater for experiments conducted at Los Alamos for the YMP.

3.0 REFERENCES

LANL-YMP-QP-02.7, Personnel Training
LANL-YMP-QP-03.5, Documenting Scientific Investigations
LANL-YMP-QP-12.3, Control of Measuring and Test Equipment and Standards
LANL-YMP-QP-17.6, Record Management

4.0 DEFINITIONS

4.1 Redox Potential

The redox potential (Eh) of a solution is a relative value which is measured as electronic potential in volts to indicate the oxidizing or reducing capability of the solution.

$Eh = P^e (2.303\ RT/F)$

P^e is the electron activity at equilibrium; $P^e = -\log \{ e \}$
R: gas constant; T: temperature: F: Faraday constant
At T = 298 K (25 °C) $Eh = 0.05916\ P^e$

4.2 Platinum Combination Redox Electrode

The platinum combination redox electrode is an electrode that combines a platinum electrode with an internal reference electrode in one glass or epoxy body.

5.0 RESPONSIBILITIES

The following personnel are responsible for the activities identified in Section 6.0 of this procedure:

- Principle Investigator (PI)
- Users of this procedure

6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this QP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified, replaced by a new document, or the current work practice is documented in accordance with QP-03.5, Section 6.1.6..

- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.

- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 Principle

The redox potential is measured with a platinum combination redox electrode which contains a noble metal, such as platinum, and a reference electrode, such as the Ag / AgC1 or calomel electrode, by using a potentiometer, such as a modern pH meter. The redox potential of a solution or groundwater is of interest because calculations from this measurement indicate what species or oxidation states of the chemical elements exist in the solution.

6.2 Equipment and Hardware / Software

- Potentiometer and Electrode

  A potentiometer is used to measure the voltage developed by a platinum combination redox electrode (voltage between a platinum redox electrode and an internal reference electrode). If a pH meter is used, it should be switched to the millivolt range. Two types of internal reference electrodes (Ag / AgC1 and calomel) may be used in the platinum combination redox electrode.

- Standard Solution

  Zobell solution should be used as the standard solution to check the performance of the platinum combination redox electrode. The theoretical redox potential values for Ag / AgC1 (with 4 M KC1 filling solution) and saturated calomel reference electrodes in Zobell solution at 25 °C are 231 and 185 millivolts, respectively. The effect of temperature on redox potential

should be calculated according to the following equation. T = temperature in °C; E = voltage in millivolts

E (Ag / AgC1) = 231 + 1.30 (25 - T)
E (calomel_ = 185 + 1.64 (25 - T)

Since the Ag / AgC1 reference was used in most platinum combination redox electrodes in the lab, the following table shows the theoretical voltage (in millivolts) of Zobell standard solution measured by Ag / AgC1 reference electrodes for temperatures between 15 and 30 °C:

Temp °C	15	16	17	18	19	20	21	22
Ag / AgC1	244	242.7	241.4	240.1	238.8	237.5	236.2	234.9

Temp °C	23	24	25	26	27	28	29	30
Ag / AgC1	233.6	232.3	231	229.7	228.4	227.1	225.8	224.5

6.2.1 Equipment Malfunctions

Malfunctions of equipment will be detectable during measurement of the Zobell standard solution. A malfunction exists if measurements do not match the values given in the table in Section 6.2.

6.2.2 Safety Considerations

Zobell solution is poisonous and should be handled and disposed of properly. The used and expired Zobell solution should be kept in a separate waste container at slightly alkaline conditions to avoid the generation of hydrocyanide gas.

6.2.3 Special Handling

For short term storage, the electrode should be kept in 0.1 M KC1 solution. If the electrode will not be used for several weeks, the electrode may be stored dry by removing filling solution from chamber followed by washing with deionized water. Zobell solution has a maximum shelf life of 30 days and should be stored in a sealed plastic bottle in a dark place below 40 °C.

6.3 Preparatory Verification

6.3.1 Hold Points

Zobell solution should be used to check the performance of the electrode and potentiometer. The checking steps in 6.5.1 must be successfully performed before any measurement of the solution may be taken.

6.3.2 Calibration

No calibration is required for the electrode and potentiometer. The effect of temperature on the redox reading is given in 6.2. The potentiometer used for the Eh measurement must have a Measuring and Test Equipment Label (see LANL-YMP-QP-12.3) which indicates the unique identification number of the meter.

6.3.3 Environmental Conditions

Ambient temperature should remain constant throughout the experiment to verify results for correct Eh measurements.

6.3.4 To minimize junction potentials, the electrode filling solution should be selected to best match the ionic strength of the solution to be measured. The filling solution level should always be at least one inch above the level of the solution being measured. If crystallization, such as AgC1 solid, is found inside the junction of Ag / AgC1 reference electrode,

deionized water or saturated KC1 solution can be used to rinse and dissolve the solid. Solvent such as acetone and alcohol can be used to clean the platinum tip. For a more thorough cleaning of the tip, the electrode should be soaked in concentrated nitric acid.

6.4 Control of Samples

Any required tracking or labeling of solutions and recording of measurements will be documented pursuant to LANL-YMP-QP-03.5.

6.5 Implementing Procedure

6.5.1 Recondition the redox combination electrode according to 6.3.4. Conduct a measurement of the Zobell standard solution to check the performance of the electrode.

6.5.1.1 If the measurement of the Zobell solution differs from theoretical voltage at a given temperature by more than ±15 mV, prepare a fresh Zobell solution. If the electrode measurements of the fresh Zobell solution still differ by more than ±15 mV, change to a new electrode.

Inform the PI if the new electrode measurements still differ by more than ±15 mV.

6.5.2 Rinse the electrode thoroughly with deionized water and remove excess water from the electrode.

6.5.2.1 The excess water can be removed by wiping the electrode gently with kimwipes.

6.5.3 Place the electrode in the solution that is to be measured. Wait until the meter reading is stabilized (usually less than five minutes) and record the Eh of the solution studies directly from the meter.

6.5.3.1 Make sure that both the platinum tip and the ceramic junction membrane of the probe are immersed in the solution being measured.

6.5.3.2 For solution with low ionic strength, it may t ake several hours to get a stable reading. A drift of less than 15 mV per hour can be considered stable. The PI should be notified if the reading is not stable within an hour.

6.5.4 Repeat section 6.5.2 and 6.5.3, if needed, to continue the Eh measurement.

6.5.5 After all solutions have been measured, repeat the measurement with Zobell solution and record the final reading in the user's notebook. This final reading from Zobell solution should not differ from theoretical voltage by more than ±15 mV.

6.5.6 Notebook Entries

The following entries must be made in the laboratory notebook:

a. Date

b. Meter identification (including MFG's name, LANL barcode number, and calibration sticker tracking number)

c. Type of redox electrode

d. Type of filling solution

e. Date Zobell solution was prepared

f. Eh of Zobell solution

g. Ambient Temperature

h. Eh obtained from sample solution

6.6 Data Acquisition and Reduction

The voltage of redox potential should be recorded to the nearest 1 millivolt or as stated on M&TE Form. The required level of precision of the data should be evaluated by the PI.

6.7 Potential Sources of Error and Uncertainty

6.7.1 The potential of cross-contamination is reduced by rinsing the electrode thoroughly between measurements.

6.7.2 Malfunctions of the meter and electrode can be detected by measuring the Eh of a fresh Zobell solution.

7.0 RECORDS

Results obtained from the proper execution of the DP are entries in the laboratory notebooks and electronic media on which data is stored. Reference LANL-YMP-QP-17.6 for submission of data as a PA record, if necessary.

8.0 ACCEPTANCE CRITERIA

Proper recording of the data specified in Section 6.5.6 constitutes the acceptance criteria for this DP.

9.0 TRAINING

YMP employees assigned to measure redox potential will be qualified by read-only training of this DP. Training should be documented in accordance with LANL-YMP-QP-02.7.

10.0 ATTACHMENTS

N / A